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Residues of Parathion and Conversion Products on Apple and Peach Foliage Resulting from Repeated Spray Applications

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Recently there has been increased concern about hazard to crop workers who enter fields or orchards following application of pesticides. In past years one of the more toxic organophosphorus pesticides, parathion (O,O-diethyl O-p-nitrophenyl phosphorothioate) has, on rare occasions, caused illness in workers exposed to residues during hand fruit thinning operations in apple orchards in the State of Washington (QUINBY and LEMMON 1958). Although such illnesses have usually occurred in workers who hand-thinned apples within 48 hours after pesticide application, we have observed many thinning operations over a period of years where workers started thinning operations within that period without reported illness. This would lead one to believe there may be factors that come into play in rare situations that may cause illness in workers in a particular orchard at a particular time under specific conditions. Studies of parathion residue poisoning outbreaks among peach pickers in California (MILBY et al. 1964) suggested that illnesses were possibly a result of residue accumulation related to total amount of parathion applied during the entire growing season. Applications had been no closer to harvest than the required 14-day interval. They felt that, although the last spraying was not the deciding factor in the causation of illness, it did contribute by adding to the already present foliage residues. Even though routine analytical capacity for the determination of the parathion oxidation product, paraoxon, was not available at that time, analysis of one leaf sample did indicate the presence of relatively large amounts of that compound. This led them to suspicion paraoxon as a likely suspect in poisoning since it is more toxic than the parent compound. In a later study of exposure of pickers in parathion-treated orange groves in California, SPEAR et al. (1974) obtained residue measurements indicating that a relatively high fraction of the residues on that crop was paraoxon.

The effect of repeated sprays on orchards in producing more hazardous conditions for crop workers has not been studied under Pacific Northwest conditions. The purpose of the present study was to determine if there is any increase in residue levels of parathion or more toxic conversion products as a result of repeated weekly applications to apple and peach trees. Alterations of parathion by photochemical, hydrolytic, and metabolic processes might lead to increased hazard to crop workers who have intimate contact with treated foliage.

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MATERIALS AND METHODS

Five apple trees were sprayed weekly throughout a 11-week period during the summer of 1972 with a conventional 0.03% parathion solution (using 25% water-wettable powder formulation). The trees were thoroughly covered to the point where the spray solution dripped from the foliage. Leaf punch samples for residue analysis were taken at 1 day and 7 days after each application. One composite sample, representing 10 leaves taken at random from each of the 5 trees, was collected at each sampling period. Similar spraying was carried out on peach trees; however, at each sampling period a composite of 50 leaf punch samples was taken at random from 3 trees. In another experiment involving 3 apple trees, levels of parathion and paraoxon residues were determined at 4, 7, 11, 14 and 34 days after application.

A clean, sharp cork borer with a diameter of 2.0 cm was used to cut sample disks from the leaves. The leaf disk samples were extracted with either 95% ethanol or benzene. The extract was filtered, dried over anhydrous sodium sulfate and stored in amber bottles until analysis. The leaf extracts were analyzed by gas liquid chromatography. A Microtek MT-220 gas chromatograph equipped with a Melpar flame photometric detector was used. Glass columns, 1.83 M x .63 cm, packed with 4% SE-30/6% QF-1 on Chromosorb W, H.P. 80/100 mesh and 5% Apiezon L on Gas Chrom Q, 80/100 mesh, were employed. Additional analyses for confirmation of paraoxon or other cholinesterase-inhibiting material were carried out by an enzymatic assay based on inhibition of rabbit serum cholinesterase. Overnight incubations were used to obtain a nearly stoichiometric loss of cholinesterase activity. Enzymatic activity was determined by the method of BENNETT et al. (1964) using acetyl thiocholine as substrate and 5,5'dithiobis (2-nitrobenzoic acid) as chromogenic reagent.

RESULTS AND DISCUSSION

Levels of residues on apple foliage at the 1- and 7-day periods following weekly spray applications are shown in Table 1. Results indicate no buildup from week to week. In fact, the highest residue values were during the first and second weeks. However, a small fraction of the higher residues at those periods could have been due to slightly heavier spray coverage during the early part of the experiment. Beyond the second week the applications were more consistent in producing a foliage wetting barely to the point of spray runoff. At 7 days after application the average parathion residues were 30% of the levels found one day after application. Calculations from the data indicate that, using first order decay, on an average half of the original residue had disappeared within approximately 3 days. Although amounts of paraoxon found were comparatively small, a decay pattern similar to the parent compound was found. In the separate experiment

TABLE 1

Residues of Parathion and Paraoxon on Apple Foliage Following 0.03% Parathion Spray Applications During June 15 to August 31[a]

Weekly periods	Days since application	Toxicant recovered (ng/cm^2)[b]		
		Parathion	Paraoxon	
			GLC method	ChE method[c]
0	pre-spray	el[d]	el[d]	el[d]
1	1	1040	30	16
	7	307	51	7
2	1	1320	48	38
	7	106	8	4
3	1	166	22	18
	7	86	14	5
4	1	202	30	23
	7	137	10	3
5	1	405	21	30
	7	210	17	7
6	1	433	27	30
	7	38	5	2
7	1	478	13	32
	7	111	9	7
8	1	255	18	32
	7	105	5	5
9	1	637	22	30
	7	115	5	6
10	1	309	22	30
	7	60	el[d]	3
11	1	495	20	26
	7	76	el[d]	7
12	1	446	19	43

[a]Hand-gun application using water-wettable powder formulation with foliage wet to runoff.
[b]Each value represents composite sample from 5 trees.
[c]Analyzed by *in vitro* cholinesterase inhibition. Expressed as paraoxon.
[d]Below lower limit of sensitivity of test.

with 3 trees, parathion residues had decayed to less than 1% of their original levels at 11 days and were not detectible at 34 days following application. At 14 days only 1 ng of paraoxon per square centimeter of leaf could be detected and at 34 days the amount was below the limit of the sensitivity of the method. No S-ethyl isomer of parathion could be detected.

In the peach foliage study involving 5 weekly applications, levels of parathion or paraoxon did not increase on that crop. As can be seen in Table 2, there was considerable reduction of parathion within each weekly period following applications. Levels of paraoxon were, in most cases, near or below the lower limit of the sensitivity of the method. As with the apple, no S-ethyl isomer of parathion could be detected. The limited data indicates that the reduction of parathion residues within the weekly periods was even greater than on the apples, which were located in the same orchard and sprayed with the same tank of spray solution at approximately the same time of day. No paraoxon was detected in spray solutions before application to the peach or apple test trees.

TABLE 2

Residues of Parathion and Paraoxon on Peach Foliage Following 0.03% Parathion Spray Applications During August 3 to August 31[a]

Weekly periods	Days since application	Toxicant recovered (ng/cm^2)[b]		
		Parathion	Paraoxon	
			GLC method	ChE method[c]
0	pre-spray	el[d]	el[d]	el[d]
1	1	340	el[d]	14
	7	29	el[d]	el[d]
2	1	150	el[d]	4.0
	7	el[d]	el[d]	0.2
3	1	452	15	13
	7	26	el[d]	0.6
4	1	318	13	10
	7	el[d]	el[d]	0.2
5	1	287	16	18

[a]Hand-gun application using water-wettable powder formulation with foliage wet to runoff.
[b]Each value represents composite sample from 3 trees.
[c]Analyzed by *in vitro* cholinesterase inhibition. Expressed as paraoxon.
[d]Below lower limit of sensitivity of test.

The average maximum daily temperature for the 11-week period during the repetitive apple foliage spraying was 30°C and the average minimum temperature 12.8°C. During the 5-week peach application period the average maximum daily temperature was 31.9°C and the average minimum was 13°C. Rainfall was minimal with traces falling during the third, fourth, fifth, and ninth week on apple and during the second and third week on peach. Sunny days were as prevalent as during an average summer. We were unable to make a direct correlation between the average weekly maximum and minimum temperatures and percent conversion of parathion to paraoxon on apple or peach foliage, or between weekly temperature and degradation of parathion on apple and peach foliage.

The data presented above indicates that under conditions of the experiment in this geographical area, which is typical of Pacific Northwest orchard conditions, there was no apparent increase in levels of parathion, paraoxon or other cholinesterase-inhibiting materials on apple or peach foliage as a result of repeated applications at weekly intervals.

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